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most layer/intervening layer/adhesive layer/intermediate layer was as close to 100:20:5:10 as possible.

The so obtained 4 kinds of sheets were sufficiently heated at 155° C. and then formed into cylindrical cups having the same configurations and unit weight as those of the cups prepared in Example 2 according to the known plug assist air-pressure forming method. For comparison, these sheets were formed into cylindrical cups having the same configurations and unit weight as above according to the sheet blow molding method as in Example 2.

Cups prepared by plug assist air-pressure forming (solid phase forming) by using EV1 as the intermediate layer-constituting resin were designated as "SR1" and cups prepared by sheet blow molding of molten sheets containing EV1 as the intermediate layer-constituting resin were designated as "SBB1". Similarly, cups formed by plug assist air-pressure forming by using EV2, EV3 and EV4 and cups formed by sheet blow molding by using EV2, and EV3 and EV4 were designated as "SPR2", "SPR3", "SPR4", "SBB2", "SBB3" and "SBB4", respectively.

With respect to each of these 8 kinds of cups, the oxygen transmission rate (QO<sub>2</sub>), haze (Hz), orientation coefficients (l, m and n), vibration resistance (N, ADN) and thickness unevenness (δL and δH) in the intermediate layer were determined in the same manner as described in Example 2 to obtain results shown in Table 8.

From the results shown in Table 8, it will readily be understood that the transparency of cups obtained in this Example is inferior to that of the cups obtained in Example 2 because of the presence of intervening layers of scraps, but a similar tendency is observed in this Example with respect to other items and cups having excellent properties can be obtained if the requirements of this invention are satisfied.

Table 8

Symbol of Cup	QO <sub>2</sub> , cc/m <sup>2</sup> · day · atm	Hz (%)	Orientation Coefficients (innermost and outermost layers)			Vibration Test Results		Thickness Unevenness in Intermediate Layer	
			γ	m	n	N	ADN	δL	δH
SPR1	1.7	12	0.32	0.10	0.58	0	0	0.19	0.09
SPR2	0.6	9	0.39	0.10	0.51	0	0	0.14	0.09
SPR3	0.6	9	0.31	0.14	0.55	0	2	0.20	0.11
SPR4	20.2	18	0.32	0.15	0.53	0	1	0.53	0.29
SBR1	3.8	26	0.03	0.01	0.96	0	1	0.21	0.13
SBR2	3.2	24	0.04	0.01	0.95	1	2	0.19	0.14
SBR3	2.8	25	0.02	0.02	0.96	1	1	0.20	0.13
SBR4	31.0	27	0.04	0.01	0.95	1	2	0.21	0.12

## EXAMPLE 7

Bottom-less laminate pipes (laminate parisons) having a symmetric 5-layer structure of outer layer/adhesive layer/oxygen-barrier layer (intermediate layer)/adhesive layer/inner layer were prepared by using an extruder for formation of intermediate layers having a diameter of 40 mm, an effective length of 880 mm and one melt channel passage, an extruder for formation of adhesive layers having a diameter of 40 mm, an effective length of 880 mm and 2 melt channel passages, an extruder for formation of outer and inner layers having a diameter of 65 mm, an effective length of 1430 mm and 2 melt channel passages and a 5-ply die for co-extrusion.

An isotactic homopolypropylene having a melt index of 0.5 g/10 min as measured according to the method of ASTM D-1238 (data of melt index given hereinafter are those as determined by the same method), a density of

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0.91 g/cc as measured according to the method of ASTM D-1505 (data of density given hereinafter are those determined by the same method) and a melting point of 165° C. as measured according to the DTA method was used as the resin constituting the outer and inner layers. A modified low density polyethylene (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a melt index of 2.0 g/10 min, a density of 0.92 g/cc, a melting point of 113° C. as measured according to the DTA method and a carbonyl group concentration of 180 millimoles per 100 g of the polymer was used as the adhesive layer-constituting resin. An ethylene-vinyl alcohol copolymer having an ethylene content of 35 mole %, a vinyl alcohol content of 64.5 mole %, a residual vinyl acetate content of 0.5 mole %, a melting point of 164° C. as measured according to the DTA method (temperature-elevating rate=10° C./min) and an oxygen permeability of  $0.16 \times 10^{-12}$  cc-cm/cm<sup>2</sup>-sec-cmHg as measured at a temperature of 37° C. and a relative humidity of 0% was used as the oxygen-barrier intermediate layer. Parisons of this multi-layer structure were designated as "parisons A".

Bottomless laminate pipes (laminate parisons) having the same symmetric 5-layer structure as described above were prepared by using the same co-extrusion equipment system as described above. The same resins as described above were used for formation of outer, inner and intermediate layers, but as the adhesive layer-constituting resin, there was employed a modified polypropylene (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a melt index of 2.0 g/10 min, a density of 0.91 g/cc, a melting point of 160° C. as measured according to the DTA method and a carbonyl group concentration of 167 millimoles per 100 g of the polymer. The pipes (parisons)

sons) were designated as "pipes B".

In each of the pipes A and B, the total thickness was about 10 mm, the inner diameter was 30 mm and the length was 30 mm, and the thickness ratio of outer layer/adhesive layer/intermediate layer/adhesive layer/inner layer was 1:1/20:1/50:1/20:1.

The pipes (parisons) A and B were heated for 35 minutes in an atmosphere maintained at  $158 \pm 0.5^\circ$  C. Both the ends of each pipe were clamped by clamps, and the pipe was drawn in the longitudinal direction. Then, the pipe was gripped by a mold for blow molding and air was introduced under pressure from one end to inflate the parison in the lateral direction. Thus, biaxially drawn blow bottles having a symmetric 5-layer structure were prepared. In the so obtained bottles, the inner diameter was 100 mm, the height is 150 mm, the average thickness of the bottle wall was 0.6 mm, the inner capacity was about 1180 cc and the unit volume

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was 0.31 dl/g. The bottles had a cylindrical shape, and it was confirmed that in each bottle, the multi-layer structure was the same as the above-mentioned structure of the parison. Bottles prepared from parisons A and from parisons B were designated as "bottles AB" and "bottles BB", respectively.

With respect to each of the so obtained bottles, the oxygen permeability ( $QO_2$ ) was determined according to the method described in Japanese Pat. Publication No. 11263/77, and the haze (Hz) was determined according to the method of JIS K-6714. Further, the bottles were subjected to the falling test described below to determine the impact resistance (SB) and delamination resistance (LB). The falling test was conducted in the following manner.

Twenty bottles were optionally chosen from each of groups AB and BB of bottles, and 1150 cc of an aqueous solution of table salt was filled in each sample bottle. The filled bottles were allowed to stand over 3 days and nights in an atmosphere maintained at  $-1^\circ\text{C}$ , and they were let to fall on a concrete floor from a height of 100 cm in an atmosphere maintained at  $20^\circ\text{C}$ , so that bottoms of the bottles hit on the concrete floor, and the falling strength (impact resistance represented by  $S_B = 100 \times [20 - S_1]/20$  in which  $S_1$  represents a number of bottles broken at the first falling test) was determined. Further, with respect to N of bottles which were not broken in the above falling test, occurrence of delamination in the bottom portion, barrel portion, shoulder portion and mouth portion was visually checked by a panel of 5 men, and the delamination resistance ( $L_B = 100 \times [N - L_1]/N$  in which  $L_1$  represents a number of bottles in which it was judged that delamination took place, among N of bottles which were not broken at the first falling test) was determined. Obtained results are shown in Table 9.

As will be apparent from the results shown in Table 9, there is no substantial difference between bottles AB and BB with respect to the oxygen permeability ( $QO_2$ ) and haze (Hz), but bottles AB are apparently excellent over bottles BB with respect to the measured values of impact strength ( $S_B$ ) and delamination resistance ( $L_B$ ). Thus, it is seen that blow bottles AB formed by heating formed pipes to melt the adhesive layer-constituting resin and then biaxially drawing the pipes are much excellent over blow bottles BB formed by conducting biaxial drawing without melting the adhesive resin layer-constituting resin with respect to the impact resistance and delamination resistance.

When pipes B were heated for 20 minutes in an atmosphere maintained at  $198 \pm 1^\circ\text{C}$ , the pipes were molten and they could not retain their shapes. Accordingly, in this case biaxial drawing was impossible.

#### EXAMPLE 9

	Bottle AB	Bottle BB
Oxygen Permeability ( $QO_2$ , cc/m <sup>2</sup> · day · atm)	10.0	10.4
Haze (Hz, %)	8.4	8.5
Impact Resistance ( $S_B$ , %)	90	60
Delamination Resistance ( $L_B$ , %)	72.2	0

#### EXAMPLE 8

Sheets having a symmetric 5-layer structure of outermost layer/adhesive layer-oxygen-barrier layer (intermediate layer)/adhesive layer/innermost layer were

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prepared by using an extruder for formation of outermost and innermost layers, which was installed with a full-flighted screw having a diameter of 65 mm and an effective length of 1430 mm and had 2 divided flow passages (melt channels), an extruder for formation of adhesive layers, which was installed with a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm and had 2 divided melt channels, an extruder for formation of intermediate layers, which was installed with a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, a 5-ply T-die having a lip width of 0.6 mm and a lip length of 500 mm and a sheet-forming machine.

The same ethylene-vinyl alcohol copolymers EV1 and EV2 as used in Example 1 and an ethylene-vinyl alcohol copolymer (EV-5) having an ethylene content of 63 mole %, a vinyl alcohol content of 37 mole %, a melting point of  $128^\circ\text{C}$ , as the DTA method described in Example 1 and an oxygen permeability of  $4.4 \times 10^{-12}$  cc-cm/cm<sup>2</sup>-sec-cmHg as measured under the conditions described in Example 1 were used as the intermediate layer-constituting resin. Low-pressure polyethylene (HDPE) having a density of 0.955 g/cc, a melting point of  $131^\circ\text{C}$ , as measured according to the DTA method and a melt index of 0.3 g/10 min as measured according to the method of JIS K-6760 and medium low-pressure polyethylene (MDPE) having a density of 0.935 g/cc, a melting point of  $122^\circ\text{C}$ , as measured according to the DTA method and a melt index of 1.0 g/10 min as measured according to the above method were used as the resin constituting the innermost and outermost layers. A modified low density polyethylene (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a density of 0.92 g/cc, a melting point of  $114^\circ\text{C}$ , as measured according to the DTA method, a melt index of 0.3 g/10 min as measured according to the above method and a carbonyl group concentration of 48 millimoles per 100 g of the polymer was used as the adhesive layer-constituting resin.

In the so formed sheets, the thickness was about 0.8 mm and the width was about 450 mm. At the sheet-forming step, the rotation rates of the screws of the three extruders were adjusted so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:5:10 as possible.

The so prepared 6 kinds of sheets were cold-rolled at room temperature at a rolling speed of about 5 m/min by using a pair of rolls having a diameter of 10 mm and a width of 500 mm. The cold-rolled sheets had a thickness of about 0.35 mm. Then, the rolled sheets were sufficiently heated in a hot air-circulated oven maintained precisely at a forming temperature indicated in Table 10. Then, the sheets were formed under a pressure of 5 to 9 Kg/cm<sup>2</sup> into rectangular trays having a length of 140 mm, a width of 100 mm and a depth of 25 mm according to the known plug assist air-pressure forming method.

For comparison, the foregoing 6 kinds of cold-rolled sheets were heated sufficiently at  $190^\circ$  or  $200^\circ\text{C}$ , and then, they were formed into rectangular trays having the same configurations as described above according to the plug assist air-pressure forming method.

With respect to each of 6 kinds of sheets before cold rolling, 6 kinds of cold-rolled sheets and 12 kinds of so prepared trays, specimens having a width of 10 mm and a length of 50 mm were cut off, the interlaminar peel strength (intermediate layer-adhesive layer and adhesive layer-adhesive layer) was measured by using a

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sive layer-innermost or outermost layer) was measured at a peeling speed of 100 mm/min in an atmosphere

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requirements of the present invention are collectively excellent.

Table 10

Sheet	Layer-Constituting Resins		Tray-Forming Temperature (°C)	Peel Strength* (g/cm width)	
	Intermediate Layer	Innermost and Outermost Layers		Intermediate layer-adhesive layer	Adhesive layer-innermost or outermost layer
Unrolled Sheet	EV1	HDPE		191	not peeled
	-	MDPE		220	-
	EV2	HDPE		119	-
	-	MDPE		184	-
	EV3	HDPE		189	-
Cold-Rolled Sheet	-	MDPE		164	-
	EV1	HDPE		1020	-
	-	MDPE		1130	-
	EV2	HDPE		1060	-
	-	MDPE		1100	-
Cold-Rolled Sheet	EV3	HDPE		1090	-
	-	MDPE		980	-
	EV1	HDPE	129	1005	-
	-	MDPE	118	130	-
	EV2	HDPE	126	655	-
	-	MDPE	118	135	-
	EV3	HDPE	129	1030	-
	-	MDPE	122	950	-
	EV1	HDPE	154	160	-
	-	MDPE	198	173	-
	EV2	HDPE	200	110	-
	-	MDPE	200	170	-
	EV3	HDPE	193	185	-
	-	MDPE	193	158	-

Sheet	Layer-Constituting Resins		Orientation Coefficients** (innermost and outermost layers)			Haze (Hz)
	Intermediate layer	Innermost and Outermost layers	l	m	n	
Unrolled Sheet	EV1	HDPE	0.02	0.01	0.97	-
	-	MDPE	0.01	0.01	0.96	-
	EV2	HDPE	0.02	0.01	0.97	-
	-	MDPE	0.01	0.02	0.98	-
	EV3	HDPE	0.01	0.01	0.96	-
Cold-Rolled Sheet	-	MDPE	0.03	0.01	0.96	-
	EV1	HDPE	0.19	0.05	0.73	-
	-	MDPE	0.17	0.09	0.74	-
	EV2	HDPE	0.21	0.06	0.73	-
	-	MDPE	0.22	0.09	0.69	-
Cold-Rolled Sheet	EV3	HDPE	0.18	0.10	0.72	-
	-	MDPE	0.19	0.07	0.74	-
	EV1	HDPE	0.19	0.11	0.70	42
	-	MDPE	0.18	0.10	0.72	30
	EV2	HDPE	0.22	0.11	0.67	-
	-	MDPE	0.23	0.09	0.68	-
	EV3	HDPE	0.19	0.10	0.71	-
	-	MDPE	0.20	0.02	0.72	-
	EV1	HDPE	0.03	0.02	0.95	78
	-	MDPE	0.02	0.04	0.94	62
	EV2	HDPE	0.04	0.03	0.93	82
	-	MDPE	0.01	0.04	0.95	51
	EV3	HDPE	0.03	0.02	0.95	79
	-	MDPE	0.04	0.03	0.93	53

Notes

\* average value (sample number = 10)

\*\* l: direction of the tray corresponds to the rolling direction of the starting sheet and to the direction of the long axis of the rectangular shape of the tray.

maintained at a temperature of 20° C. and a relative humidity of 60%, and the orientation coefficients (l, m and n) of the intermediate layer were determined according to the fluorescent method described hereinbefore. Further, with respect to 12 kinds of the resulting trays, the haze (Hz) was determined according to the method of JIS K-6714. Test results are shown in Table 10.

As will be apparent from the results shown in Table 10, trays prepared from resin combinations HDPE-EV1, HDPE-EV2 and MDPE-EV3 meeting the re-

## EXAMPLE 9

Symmetric 5-layer sheets having a thickness of 0.8 mm and a width of 450 mm were formed by using the extruding and sheet-forming equipment system described in Example 8. The rotation numbers of the screws were adjusted as in Example 8 so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:5:10 as possible.

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The same ethylene-vinyl alcohol copolymers EV1 and EV2 as used in Example 1 were used as the intermediate layer-constituting resin. Polybutene-1 having a density of 0.915 g/cc, a melting point of 129° C. as

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cluding EV1 as the intermediate layer constituting resin and meeting the requirements of the present invention are used and the forming temperature is adjusted to 125° C.

Table 11

Intermediate Layer-Consti- tuting Resin	Forming Temperature (°C)	Oxygen Permeability(O <sub>2</sub> ) (cc/m <sup>2</sup> · day · atm)	Falling Strength (S <sub>g</sub> ) (%)	Delamination Resistance (L <sub>d</sub> ) (%)
EV1	125	1.2	100	100
EV2	125	0.4	90	92.9
EV1	200	2.1	80	87.5
EV2	200	0.3	70	71.4

measured according to the DTA method and a melt flow index of 0.1 g/10 min as measured according to the method of ASTM D1238 (condition E) was used as the resin constituting the innermost and outermost layers.

A modified ethylene-vinyl acetate copolymer (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a density of 0.94 g/cc, a melting point of 93° C. as measured according to the DTA method, a melt index of 2.0 g/10 min as measured according to the method of JIS K-6760 and a carbonyl group concentration of 240 millimoles per 100 g of the polymer was used as the resin constituting the adhesive layer between the intermediate layer and the innermost or outermost layer.

Two kinds of the so prepared sheets were sufficiently heated in a hot air-circulated oven maintained precisely at a forming temperature indicated in Table 11 and installed with an infrared heater, and then, they were formed into cylindrical cups having a diameter of 85 mm, a height of 50 mm, an inner capacity of 300 cc and a unit weight of 9 to 10 g per cup according to the known plug assist air-pressure forming method.

For comparison, the foregoing 2 kinds of sheets were sufficiently heated at 190° to 200° C. in the above-mentioned oven and they were formed into cylindrical cups having the same dimensions as described above according to plug assist air-pressure forming method.

With respect to each of the so prepared 4 kinds of cups, the oxygen permeability (QO<sub>2</sub>) was determined according to the method described in Example 7. Ten cups were chosen from each of the foregoing 4 kinds of cups, and 340 g of an aqueous solution of table salt was filled in each cup and an aluminum lid was attached to each cup by means of a seamer. Then, the cups were allowed to stand in an atmosphere maintained at -1° C. over three days and nights, and immediately, they were let to fall on a concrete floor from a height of 3 mm in an atmosphere maintained at 20° C. so that the bottoms hit on the concrete floor. The falling strength (S<sub>g</sub>) was calculated according to the method described in Example 7, and the delamination resistance (L<sub>d</sub> defined in Example 7) was visually evaluated by a panel of 5 men. Obtained results are shown in Table 11.

As will be apparent from the results shown in Table 11, cups excellent in oxygen-barrier property and falling strength can be obtained when resin combinations in-

## EXAMPLE 10

Symmetric 5-layer sheets having a thickness of about 0.8 mm and a width of 450 mm were formed by using the extruding and sheet-forming equipment system described in Example 8. The rotation numbers of the screws of the extruders were adjusted so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:5:10 as possible.

The same ethylene-vinyl alcohol copolymers EV1, EV2 and EV5 as used in Example 8 were employed as the intermediate layer-constituting resin. A polycarbonate (PC) synthesized from phosgene and bisphenol-A, which had a softening point of 160° C. as measured according to the torsion rigidity measurement method, and poly(methyl methacrylate) (PMMA) having a glass transition temperature of 115° C. as measured according to the DTA method were used as the resin constituting the innermost and outermost layers. The same modified ethylene-vinyl acetate copolymer as used in Example 8 was used as the resin constituting the adhesive layer between the intermediate layer and the innermost or outermost layer.

The so prepared 6 kinds of sheets were formed into cylindrical cups having the same configurations and unit weight as those of the cups prepared in Example 9 at a forming temperature indicated in Table 12 according to the known plug assist air-pressure forming method.

With respect to each of the so formed 6 kinds of cups, the orientation coefficients (l, m and n) of the intermediate layer were determined according to the above-mentioned fluorescence method, the interlaminar peel strength between the intermediate layer and adhesive layer was measured according to the method described in Example 8, and the thickness unevenness (standard deviations  $\delta L$  and  $\delta H$ ) in the vertical direction and circumferential direction of the cup was determined. Obtained results are shown in Table 12.

From the results shown in Table 12, it will readily be understood that when resin combinations meeting the requirements of the present invention are employed, cups collectively excellent in various properties can be obtained.

Table 12

Layer-constituting Resins	Forming Temperature (°C)	Orientation Coefficients			Thickness Uniformity in Cup		Peel Strength (g/cm width) (intermediate layer-adhesive layer)
		l	m	n	$\delta L$	$\delta H$	
EV1 PC	153	0.32	0.10	0.58	0.18	0.07	480
EV3 PC	153	0.29	0.12	0.59	0.20	0.10	<10
EV5 PC	153	0.30	0.09	0.61	0.19	0.15	235
EV1 PMMA	105	0.25	0.09	0.26	0.23	0.06	253



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Table 12-continued

Layer-constituting Resins	Forming Intermediate Layer	Temperature (°C.)	Orientation Coefficients			Thickness Uniformity in Cup		Tensile Strength (g/cm width) (intermediate layer-adhesive layer)
			l	m	n	8L	8H	
EV3	PMMA	105	0.27	0.06	0.67	0.25	0.12	<10
EV5	PMMA	105	0.23	0.07	0.70	0.21	0.14	135

What we claim is:

1. A transparent multi-layer varied thickness container obtained by draw-forming a parison composed of a coextrudate of at least one oxygen barrier thermoplastic resin layer and at least one crystalline polyolefin layer, said oxygen barrier thermoplastic resin having an oxygen permeability lower than  $5.5 \times 10^{-12}$  cc-cm/cm<sup>2</sup>-sec-cmHg as measured at 37° C. and being selected from the group consisting of a copolymer consisting essentially of ethylene and vinyl alcohol and a polyamide, wherein said oxygen barrier thermoplastic resin and said polyolefin are selected so that the requirement represented by the following formula:

$$|T_B - T_O| \leq 35^\circ \text{C.}$$

wherein  $T_B$  stands for the melting or softening point (°C.) of said oxygen-barrier thermoplastic resin and  $T_O$  stands for the melting or softening point (°C.) of said polyolefin, is satisfied, and wherein at least one of two-dimensional orientation coefficients (l and m) of at least one layer composed of said polyolefin in a smallest-thickness portion of the container is at least 0.05.

2. A container as set forth in claim 1 wherein the oxygen barrier thermoplastic resin is an ethylene/vinyl alcohol copolymer containing vinyl alcohol units at a content satisfying the requirement represented by the following formula:

$$0.61T_O - 56.8 \leq X \leq 0.61T_O - 24.2$$

wherein  $T_O$  stands for the melting or softening point (°C.) of the polyolefin and X stands for the content (mole %) of the vinyl alcohol units in the oxygen barrier thermoplastic resin.

3. A container as set forth in claim 1 wherein the oxygen barrier thermoplastic resin and the polyolefin are selected so that the requirement represented by the following formula:

$$|T_B - T_O| \leq 10^\circ \text{C.}$$

wherein  $T_B$  and  $T_O$  are as defined above, is satisfied, at least one of two-dimensional orientation coefficients (l and m) of at least one layer of the polyolefin in a smallest-thickness portion of the container is at least 0.1, each resin layer has a haze (Hz) lower than 10%, and wherein the bonding strength between every two adjacent layers is at least 20 g/cm.

4. A container as set forth in claim 1 wherein the polyolefin is a crystalline polypropylene or a crystalline ethylene-propylene copolymer having an ethylene content of 1 to 20 mole %.

5. A container as set forth in claim 1 wherein the polyolefin is present on both the surfaces of the container as the outermost and innermost layers and the oxygen barrier thermoplastic resin is present as the intermediate layer of the container.

6. A transparent multi-layer varied thickness container obtained by draw-forming a parison composed of a co-extrudate of at least one layer composed of (A) an oxygen barrier thermoplastic resin having an oxygen permeability lower than  $5.5 \times 10^{-12}$  cc-cm/cm<sup>2</sup>-sec-cmHg as measured at 37° C., at least one layer

comprising (B) a crystalline polyolefin and at least one layer interposed between said oxygen barrier thermoplastic resin layer and said polyolefin layer and being composed of (C) a resin having an adhesiveness to both of said resins, said oxygen barrier thermoplastic resin being selected from the group consisting of a copolymer consisting essentially of ethylene and vinyl alcohol and a polyamide; said adhesive resin being a polyolefin modified with at least one ethylenically unsaturated monomer selected from the group consisting of unsaturated carboxylic acids and anhydrides, esters and amides thereof containing carbonyl groups at a concentration of 10 to 1400 millimols per 100 g of the polymer, wherein said three resins are selected to that the requirements represented by the following formulae:

$$|T_B - T_O| \leq 35^\circ \text{C.}$$

and

$$90^\circ \text{C.} \geq T_O - T_C \geq 27^\circ \text{C.}$$

wherein  $T_B$  stands for the melting or softening point (°C.) of said oxygen-barrier thermoplastic resin,  $T_O$  stands for the melting or softening point (°C.) of said polyolefin and  $T_C$  stands for the melting or softening point (°C.) of said adhesive resin, at least one of two-dimensional orientation coefficients (l and m) of at least one layer composed of said polyolefin in a smallest-thickness portion of the container is at least 0.05, and wherein the layer of said adhesive resin is substantially non-oriented.

7. A container as set forth in claim 6 wherein the polyolefin (B) is a crystalline polypropylene or a crystalline ethylene-propylene copolymer having an ethylene content of 1 to 20 mole %, the layer comprising said polyolefin is present on both the surfaces of the container as the outermost and innermost layers, the oxygen barrier thermoplastic resin (A) is a copolymer consisting essentially of ethylene and vinyl alcohol and containing vinyl alcohol units at a content satisfying the requirement represented by the following formula:

$$0.61T_O - 56.8 \leq X \leq 0.61T_O - 24.2$$

wherein  $T_O$  stands for the melting or softening point (°C.) of the polyolefin (B) and X stands for the content (mole %) of the vinyl alcohol units in the oxygen barrier thermoplastic resin (A), the layer of said oxygen barrier thermoplastic resin is present as the intermediate layer of the container, the adhesive resin (C) is present as the adhesive layer interposed between the outer surface layer and the intermediate layer and as the adhesive layer interposed between the inner surface layer and the intermediate layer, and wherein the thickness ratio of the respective resin layers is in the following range:

$$(B):(A) = \text{from } 1:1 \text{ to } 500:1 \text{ and}$$

$$(B):(C) = \text{from } 1:1 \text{ to } 500:1.$$

8. A container as set forth in claim 6 which is a biaxially drawn plastic bottle.

9. A container as set forth in claim 6 which is a draw-formed plastic cup.



## United States Patent [19]

Christensen et al.

[11] 4,405,667

[45] Sep. 20, 1983

## [54] RETORTABLE PACKAGING STRUCTURE

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428/475.8, 476.1, 516; 523; 206/484, 484.2,  
206/548.2; 426/113, 127

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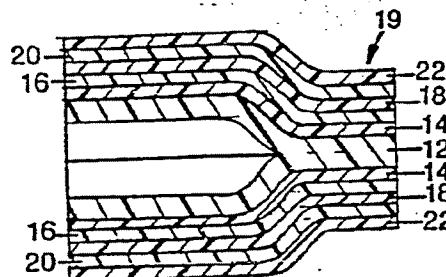
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Primary Examiner—William J. Van Balen  
Attorney, Agent, or Firm—Stuart S. Bowin; Thomas D.  
Wilhelm

## [57] ABSTRACT

A retortable pouch is made without the use of metal foil. The improved heat sealable structure has an inner heat seal layer of linear low density polyethylene. The second, or adjacent layer is a blend of 20% to 80% linear low density polyethylene and 80% to 20% propylene ethylene copolymer. Optional third, fourth and fifth layers are propylene ethylene copolymer. A sixth layer is anhydride modified polypropylene. A seventh layer is nylon, the eighth layer is ethylene vinyl alcohol copolymer and the ninth layer is nylon. The entire multiple layer structure is firmly adhered together so that the layers mutually support each other in the unitary package.

9 Claims, 6 Drawing Figures



U.S. Patent

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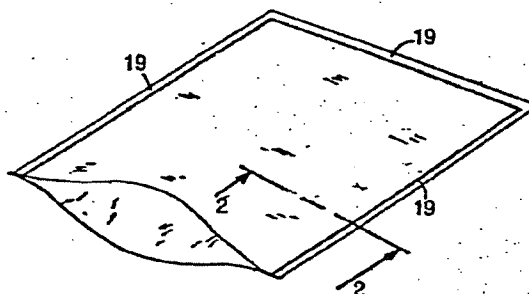


FIG. 1

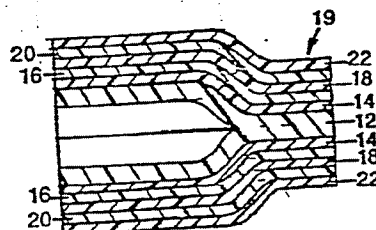


FIG. 2

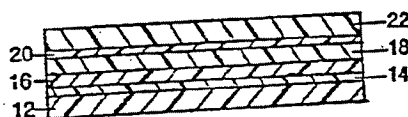


FIG. 3



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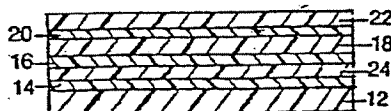


FIG. 4

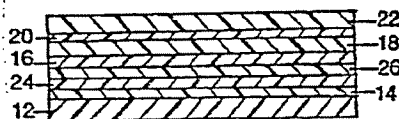


FIG. 5

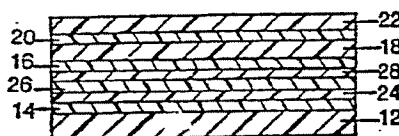


FIG. 6

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## RETORTABLE PACKAGING STRUCTURE

## BACKGROUND OF THE INVENTION

Heat sealed pouches made from flexible sheet stock are now being used for packaging certain products which are stored under sterile conditions. Typical products packaged and used in this manner are certain foods and medical supplies. The packaging thus used is known generally as a retort pouch.

The first generation of retort pouches included certain adhesives, used for laminating the various layers. The adhesives had some residual monomer moieties after the adhesive was fully cured. These structures were rejected by governmental authorities because of the perceived possibility of migration of toxic monomers into the packaged food product.

In more recent developments, retort pouch structures are made by various methods of adhering the layers to each other by one or more of several extrusion processes. Illustrative of these processes is one taught in United States Patent 4,190,477. In the process described in that patent, biaxially oriented polyester is first adhesively mounted to metal foil on what is to be the outside of the package. This use of adhesive is considered acceptable because the foil serves as an effective barrier to migration of residual monomer, from the adhesive, to the inside of the package. A polypropylene-based heat sealing layer is separately extruded. A primer is applied to the side of the foil opposite the polyester. Finally the sealant layer and the primed foil are extrusion laminated together using an extrusion grade polypropylene-based polymer as the extrusion laminant.

Common to the requirements of retort pouch packaging is the requirement that the filled and sealed package be subjected to sterilizing conditions of relatively high temperature after the pouch is filled with product and sealed. Typical sterilizing conditions range in severity up to about 275° F. with residence times at that temperature of as much as 30 minutes or more. Such conditions impose severe stresses on the packages. Many packaging structures provide excellent protection for the package contents at less severe conditions. For example, relatively simple packaging structures for packaging requiring the ability to withstand boiling water, such as at 212° F. are readily available from several suppliers. When sterilizing conditions are required, however, most of these packages fail to survive the processing. Typically, problems are encountered with excessive weakening or failure of the heat seals about the periphery of the pouch. Also, certain weaknesses or separations may develop between the layers in the multiple layer sheet structure.

In some sterile packaging applications, it is desirable to be able to visibly inspect the product. In these cases, a transparent packaging film is highly desirable, and foil based films are less desirable.

In other packaging applications, it is indeed important that metal foil be specifically excluded from the structure so that the completed package can be penetrated by microwave energy, such as for cooking contained food.

Among those structures which have proven themselves capable of withstanding the sterilizing process, the sealant, or inner layer of the pouch is believed to be, in almost all cases, based on polypropylene, and in some cases, propylene copolymers. While pouches made with the propylene based polymers are functionally capable

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of surviving the sterilizing process, their sheet structure is relatively brittle and hard. Thus the pouches are somewhat susceptible to cracking and crazing if subjected to rough handling. There are also some limited problems with weakening of interlayer adhesion between the layers. Once the interlayer adhesion is weakened, the pouch is, of course, subject to further damage by limited abusive handling which an unweakened pouch could normally tolerate.

While pouches made with known sheet structures have achieved a limited degree of success, it is desirable to provide an improved sheet structure which is capable of surviving intact the typical sterilizing processes. It is particularly desirable to have a sheet structure with an improved sealant layer structure. In some cases, it is desirable that the sheet structure be transparent. In still other cases, it is specifically important that the sheet structure contain no significant metallic component.

Among the characteristics of the improved sealant layer structure are that it should be less brittle than the propylene-based sealants. It should also survive the sterilizing process with good heat seal strength about the pouch periphery. Also the interlayer adhesion should remain strong enough that the several layers remain intact as a unit and mutually support each other under stress, particularly after the sterilization process.

## SUMMARY OF THE INVENTION

It has now been found that certain of these and related objectives are met in a novel multiple layer flexible packaging film structure, herein disclosed. The layers are firmly adhered to each other in face to face contact. The structure includes, in order, a first layer of linear low density polyethylene and a second layer of a blend of 20% to 80% linear low density polyethylene and 80% to 20% propylene ethylene copolymer.

Optionally, there are one or more of third, fourth and fifth layers of propylene ethylene copolymer. A sixth layer is anhydride modified polypropylene, with seventh, eighth and ninth layers of nylon, ethylene vinyl alcohol copolymer, and nylon respectively. In a preferred embodiment, the composition of the second layer is 40% to 60% linear low density polyethylene and 60% to 40% propylene ethylene copolymer.

The structures of this invention may be assembled by a variety of processes, the specific choice of a process depending on the equipments available and the exact polymers chosen. In most cases, the sixth through ninth layers will first be made into a subassembly, and then the balance of the structure added. While the process of assembling the sub-assembly of layers six through nine is not critical, a typical and most economical process is coextrusion of the subassembly structure.

One acceptable process of completing the structure is extrusion laminating the first, second and third layers to a fifth layer, using the fourth layer as the extrusion laminant. Another includes the process of extrusion laminating the first, second and third layers to the sixth layer using the fourth layer as the extrusion laminant. Yet another includes the process of extrusion laminating the first and second layers to the sixth layer using the third layer as the extrusion laminant.

Still another acceptable process includes extrusion laminating the first layer to the sixth layer using the second layer as the extrusion laminant.

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In yet another process, the first layer is coextrusion laminated to the sixth layer using as the laminant a coextrusion of the second and third layers.

Finally, the process of making the structure may be completed by extrusion coating the first and second layers onto the sixth layer.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a pouch, sealed on three sides, and made with the sheet structures of this invention.

FIG. 2 shows a cross-section of the pouch of FIG. 1 taken at 2-2 of FIG. 1.

FIG. 3 shows a cross-section of the sheet structure used to make the pouch of FIG. 1.

FIGS. 4, 5, and 6 show cross-sections of alternate sheet structures of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The invention will now be described in detail and in relation to the drawings. FIG. 1 illustrates a pouch such as is the desired useful packaging structure of this invention. A cross-section of a portion of the pouch is shown in FIG. 2. The sheet material used to make the pouch is seen in FIG. 3. By comparison of FIGS. 2 and 3 it is seen that the FIG. 2 construction consists of two sheet elements of the FIG. 3 construction in face to face relation with the layers 12 joined at the one edge. The pouch is formed by arranging the two sheet elements in face to face relationship and forming heat seals 19 about the common periphery. Alternately, the pouch may be formed by folding a sheet element onto itself and forming heat seals about the edges. Either way, the formed pouch appears as shown in FIG. 1.

Referring now to FIGS. 2 and 3, layer 12 is a heat sealable layer comprised of linear low density polyethylene. Layer 14 is an adhesive, or tie, layer and is a blend of linear low density polyethylene and propylene ethylene copolymer. Layer 16 is also an adhesive, or tie, layer and is an anhydride modified polypropylene. Layers 18 and 22 are nylon. Layer 20 is an ethylene vinyl alcohol copolymer. The formed pouch structure thus has an inner heat seal layer of linear low density polyethylene and an outer surface of nylon. The intermediate layers serve the functions of strengthening the structure, providing certain barrier properties, and bonding the structure together.

The formed pouch is intended for packaging products which will be subjected to a sterilizing process after the product is in the package and the package is sealed. A common sterilizing process is known as autoclave, or retort, processing. In this process, closed and sealed packages are placed in a pressure vessel. Steam and water are then introduced into the vessel at about 275° F. at a sufficiently high pressure to permit maintenance of the desired temperature. The temperature and pressure are usually maintained for about 30 minutes. Finally, the pressure vessel and product are cooled at the same process pressure, after which the pressure is released and the processed packages are removed.

In the pouch structure, the heat seal layer 12 significantly influences the physical properties of the pouch because there is physically more material in layer 12 than in any other single layer. The composition of layer 12 may be any of the polymers or copolymers known as linear low density polyethylene. These polymers are relatively extensible and elastic in nature, giving the

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pouch a degree of resilience in absorbing physical abuse.

Layer 14 is a blend of 80% to 20% propylene ethylene copolymer and 20% to 80% linear low density polyethylene. A preferred blend is 60% to 40% propylene ethylene copolymer and 40% to 60% linear low density polyethylene. The blend of layer 14 serves as a tie layer to bond layer 12 to the remainder of the structure.

Layer 16 is an anhydride modified polypropylene. Two preferred materials, which are modified with maleic anhydride, are available from Mitsui Company of Japan as Admer QF500 and Admer QF500X.

The nylons in layers 18 and 22 usually are the same composition, although the user may satisfactorily choose to use different nylon polymers. Preferred nylon compositions are nylon 6 and blends of nylon 6 with nylon 12. In the blends, no more than 50% of the composition may be nylon 12, since concentrations over this amount yield pouches susceptible to failing abuse testing after retort processing.

Layers 18 and 22 provide, as their primary function, abuse resistance. Since nylon polymers can absorb a lot of abuse, they protect the more physically sensitive layers of the pouch structure. Layer 22 is specifically protective of the thin, brittle, and fragile layer 20 of ethylene vinyl alcohol. The combination of layers 18 and 22 serves to encapsulate layer 20 during the extrusion process, and thus provides a degree of thermal protection in that role.

Layer 20 of ethylene vinyl alcohol copolymer provides a barrier to passage of oxygen through the pouch structure. Any of the ethylene vinyl alcohols may be used, so long as at least 90% of the ester units have been hydrolyzed to the alcohol form. While some ethylene vinyl alcohol copolymers may provide an adequate barrier with less than 90% hydrolysis, this normally is not the case, and the composition of layer 20 must be chosen such that the needed barrier is provided. Because the vinyl alcohol is so brittle, it is sometimes desirable to incorporate plasticizing agents into layer 20. And such is entirely acceptable so long as an adequate oxygen barrier property is preserved.

FIG. 4 shows a cross-section of an alternate sheet structure of the invention. The FIG. 4 structure is the same as the FIG. 3 structure except that it incorporates one additional layer 24 of propylene ethylene copolymer between layers 14 and 16. The FIG. 5 structure is the same as the FIG. 3 structure, with the addition of two layers 24 and 26 of propylene ethylene copolymer. Finally, the FIG. 6 structure is the same as the FIG. 3 structure, with the addition of three layers 24, 26, and 28 of propylene ethylene copolymer.

In any given structure where more than one of layers 24, 26 and 28 are used, the compositions of the respective layers may, but normally will not, be the same. For example, in the construction of the FIG. 5 structure, it is convenient to first coextrude two structure subassemblies. The first subassembly includes layers 16, 18, 20 and 22. The second subassembly includes layers 12, 14 and 24. The structure is then fully assembled by joining layers 16 and 24 in an extrusion lamination process using a propylene ethylene copolymer, layer 26, as the extrusion laminant. Thus the process requirements for layer 24, for coextrusion, may differ significantly from the process requirement for layer 26, for extrusion lamination. In accommodation of those process differences, different specific polymers may be selected. Similarly,

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within the limits of the process requirements, the compositions of layers 24, 26, and 28 may be selected or adjusted in order to improve bond strength with adjacent layers. Thus, for example, the composition of layer 28 may be adjusted to provide improved bonding to layer 16. Or it may be adjusted to accommodate improved bonding to layer 26. Clearly, in structures this complex, a multitude of options are available, and minor adjustments may be made, without departing from the spirit of the invention.

Blend layer 14 is intentionally defined with a broad range of compositions such that the composition for each structure may be tailored for best performance in that particular structure.

The first important parameter to be considered is that the two components of the blend must form a compatible polymeric mixture, which they do. Secondly each of the components of the blend contributes to forming good bonding with the adjacent layer of like polymeric composition. Thus the propylene ethylene copolymer component of the blend contributes the preponderance of the bond forming capability between layer 14 and the adjacent propylene-based layer. Similarly the linear low density polyethylene component of the blend contributes the preponderance of the bond forming capability between layer 14 and layer 12 which is composed of linear low density polyethylene.

In general terms, the preferred composition for layer 14 is 40% to 60% propylene ethylene copolymer and 60% to 40% linear low density polyethylene. Indeed, a composition highly satisfactory for a variety of structures of this invention is 50% propylene ethylene copolymer and 50% linear low density polyethylene. Depending which polymers or copolymers are independently chosen for layers 12, 14, and the adjacent propylene based layer, i.e. 16 or 24, the blend composition may be adjusted for maximum benefit either by adjusting the blend ratio, by selecting an alternate polymer component of propylene ethylene copolymer or of linear low density polyethylene, or by using both techniques. For example, using the general structure of FIG. 3, if the bond between layers 14 and 16 is weaker than desired, the composition of layer 14 may be adjusted. One alternative is to increase the proportion of propylene ethylene copolymer in the layer 14 composition. Another alternative is to choose an alternate specific polymer for use as the propylene ethylene component of the blend.

The above techniques regarding adjusting the layer 14 composition are significant in enabling the best practice of the invention and in obtaining maximum benefit from the packages of the invention. These techniques are, however, only significant regarding maximizing the benefits to be gained from the invention, and are not critical to the basic practice of the invention, which can be satisfactorily practiced with a broad range of compositions of layer 14.

The term propylene ethylene copolymer should herein be interpreted, and is intended to include, copolymers of propylene and ethylene, blends of polypropylene and polyethylene, and combinations of copolymers and blends.

As used in the structure, layers 14, 16, 24, 26, and 28, which have polypropylene-based compositions, do also contain some ethylene. The function of the ethylene is to provide increased resilience to the layers between layer 18 and the sealant layer, and to lend an increased degree of tolerance to bending of the pouch. In general,

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polypropylene homopolymer layers are susceptible to developing lines of stress weakening when subjected to abuse testing or abusive handling. The ethylene component reduces this susceptibility. It should be noted, however, that not every propylene-based layer need contain ethylene if an adjacent layer does have extensible properties. In that case the adjacent layer may absorb the abuse through the layer interface. Layer 16, for example, is chosen for its bonding properties, and it may or may not contain ethylene. Normally the adjacent layer, such as layer 14 in the FIG. 3 structure, or layer 28 in the FIG. 6 structure will contain ethylene and provide the necessary resilience. However, where possible, at least a minimal ethylene content is desirable. A lower limit of about 2% ethylene is preferred to provide minimal improvements in the layers. A composition of 3.5% ethylene is highly desirable. As the amount of ethylene is increased, the susceptibility to stress weakening is reduced. However, the ethylene content may not be indiscriminantly increased, as other, and undesirable, parameters may emerge. Particularly, polymeric ethylene does not tolerate retort conditions as well as polypropylene, so a preponderance of polypropylene is required for processability. Also a high fraction of polypropylene is necessary for good bonding, such as to layer 16. For most uses, the ethylene content will be relatively low. The specific content for each layer and each structure depends upon the end use anticipated for the final structure.

Another primary element of concern is that the compositions of layers 14, 24, 26, and 28 be selected such that there is good compatibility physically and chemically between the compositions of layers which are joining at a common interface; this to encourage intimate contact and bond development between the respective components of the layers.

The sheet structures of this invention may be made by a variety of processes and combinations of processes. The process and its sequences may be selected according to the equipment and polymers available. The specific structure selected and the layer 14 composition will be at least partially dependent on the process and its sequences.

Using FIG. 3 as an example structure, layers 16, 18, 20 and 22 are coextruded as a four-layer film. Finally the structure is completed by extrusion coating or coextrusion coating layers 14 and 12 onto layer 16. Use of this process imposes certain limitations on the composition of layer 14. While it must bond to layer 16 in the finished structure, a primary concern imposed by the process is that the compositions of layer 12, and particularly, 14 must be coselected to that the processing temperatures and melt flow properties are compatible to extrusion coating, coextrusion and coextrusion coating, as the specific process may require. Particularly regarding layer 14, certain compromises, such as bond strength between layers 14 and 16, may have to be made in its composition, albeit within the ranges of the invention, in order to accommodate the coextrusion and extrusion coating processes.

In another process for making the FIG. 3 structure, layer 12 is extruded as a separate film. Layers 16, 18, 20 and 22 are coextruded as a separate film subassembly of the structure. Layer 12 and the combination of layers 16, 18, 20, and 22 are then simultaneously pulled through a nip from opposite sides and layer 14 is extruded into the nip between layers 12 and 16 in an extrusion lamination process.



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In still another process for making the structure of FIG. 3, layers 12 and 14 are coextruded and the combinations of layers 12 and 14, and a coextruded subassembly of layers 16, 18, 20, and 22 are pulled through a hot nip from opposite sides, and a combination of heat and pressure are applied to effect the formation of the bond between layers 14 and 16.

Now that these several exemplary processes for making the structure of FIG. 1 have been described, those skilled in the art will appreciate that the structures illustrated in FIGS. 4, 5, and 6 may likewise be made by similar processes and combinations of processes.

Further to illustrate the processes which may be involved in making the more complex structures, additional process sequences are hereinafter iterated.

First referring to FIG. 6: Layers 28, 16, 18, 20 and 22 are coextruded as a multiple layer subassembly film. Layers 12, 14 and 24 are also coextruded as a separate multiple layer subassembly film. Finally, the two subassemblies are joined in an extrusion lamination process to make the finished assembly, using the layer 26 composition as the extrusion laminant.

Second referring to FIG. 5: Layers 16, 18, 20 and 22 are coextruded as a multiple layer subassembly film. Layers 12, 14, and 24 are coextruded as a separate multiple layer subassembly film. Finally, the two subassemblies are joined in an extrusion lamination process to make the finished assembly, using the layer 26 composition as the extrusion laminant.

Thirdly referring to FIG. 4: Layers 16, 18, 20 and 22 are coextruded as a multiple layer subassembly film. Layers 12 and 14 are coextruded as a separate multiple layer subassembly film. The two subassemblies are joined in an extrusion lamination process to make the finished assembly, using the layer 24 composition as the extrusion laminant.

Having thus described the invention, what is claimed is:

1. A multiple layer flexible packaging structure, wherein the layers are firmly adhered to each other in face to face contact, the structure comprising, in order:

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- (a) a first layer of linear low density polyethylene;
- (b) a second layer of a blend of 20% to 80% linear low density polyethylene and 80% to 20% propylene ethylene copolymer;
- (c) optionally, one or more of third, fourth and fifth layers of propylene ethylene copolymer;
- (d) a sixth layer of anhydride modified polypropylene;
- (e) a seventh layer of nylon;
- (f) an eighth layer of ethylene vinyl alcohol copolymer; and
- (g) a ninth layer of nylon.

2. A structure as in claim 1 wherein the composition of said second layer is 40% to 60% linear low density polyethylene and 60% to 40% propylene ethylene copolymer.

3. A structure as in claim 1 made by the process of extrusion laminating said first, second and third layers to a fifth layer, using said fourth layer as the extrusion laminant.

4. A structure as in claim 1 made by the process of extrusion laminating said first, second, third and fourth layers to said sixth layer using said fifth layer as the extrusion laminant.

5. A structure as in claim 1 made by the process of extrusion laminating said first and second layers to said sixth layer using said third layer as the extrusion laminant.

6. A structure as in claim 1 made by the process of extrusion laminating said first layer to said sixth layer using said second layer as the extrusion laminant.

7. A structure as in claim 1 made by the process of coextrusion laminating said first layer to said sixth layer using as the laminant a coextrusion of said second and third layers.

8. A structure as in claim 1 made by the process of extrusion coating said first and second layers onto said sixth layer.

9. A pouch made from the packaging structure of claim 1 or 2.

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SHOE COY (612 B) + 622  
SUBJ. COE

# United States Patent [19]

Foster

[11] Patent Number: 4,561,920

[45] Date of Patent: Dec. 31, 1985

## [54] BIAXIALLY ORIENTED OXYGEN AND MOISTURE BARRIER FILM

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[73] Assignee: Norchem, Inc. formerly Northern Petrochemical Company, Omaha, Nebr.

[21] Appl. No.: 578,073

[22] Filed: Feb. 8, 1984

[51] Int. Cl.<sup>4</sup> ..... B32B 31/00

[52] U.S. Cl. .... 156/244.11; 156/244.24; 428/35; 428/516; 428/518; 428/349

[58] Field of Search ..... 428/35, 516, 349; 156/244.11, 244.24

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Primary Examiner—Edith Buffalow  
Attorney, Agent, or Firm—Donald F. Haas

### [57] ABSTRACT

A biaxially oriented oxygen and moisture barrier film and a method of producing such a film which comprises co-extruding at least one polyolefin polyolefin layer, at least one layer of an ethylene vinyl alcohol copolymer with a melt flow rate of at least about 8 grams per 10 minutes, and an adhesive layer wherein the layers are combined into a composite sheet with the adhesive interposed between the polyolefin layer and ethylene vinyl alcohol copolymer layers. Next, the composite sheet is immediately cooled so that the crystallinity of the ethylene vinyl alcohol copolymer is no more than about 25 percent. Finally, the composite sheet is biaxially oriented in the longitudinal direction to a degree of about 2:1 to about 4:1 and in the transverse direction to a degree of about 3:1 to about 7:1.

14 Claims, No Drawings

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## BIAXIALLY ORIENTED OXYGEN AND MOISTURE BARRIER FILM

### BACKGROUND OF THE INVENTION

The present invention relates to a method for producing a biaxially oriented oxygen and moisture barrier film which is comprised of a polyolefin layer and an ethylene vinyl alcohol copolymer barrier layer. More particularly, the invention relates to a simple continuous method whereby the two layers are combined by co-extrusion and biaxially oriented at the same time.

Ethylene vinyl alcohol copolymer resins offer excellent barrier properties with respect to such gases as oxygen, carbon dioxide and nitrogen. In addition, they are also effective barriers against odors and the loss of flavor. Such resins, hereinafter referred to as EVOH resins, are moisture sensitive and the barrier properties are reduced in the presence of high humidity. Polypropylene offers excellent barrier properties with respect to moisture together with good strength properties and a high use temperature. When EVOH resins are encapsulated by layers of polypropylene, they are protected from moisture and therefore retain their barrier characteristics.

The biaxial orientation of EVOH resins enhances their barrier properties as well as reduces their susceptibility to moisture. The biaxial orientation of polypropylene increases its stiffness and enhances both its optical and other physical properties such as tensile strength, tear strength, and other mechanical properties.

In the past, others have attempted to produce biaxially oriented composite structures containing both polypropylene and EVOH resins by first producing a polypropylene sheet and orienting the sheet in the longitudinal direction. Then a layer of EVOH resin was either laminated or extrusion coated onto the polypropylene and the composite was then oriented in the transverse direction. This method of production is costly and only results in the orientation of the EVOH resin in one direction, thus not achieving the full benefit of biaxial orientation.

U.S. Pat. No. 4,239,826, issued Dec. 16, 1980, discloses a multi-layer barrier film comprising a barrier layer of substantially pure ethylene vinyl alcohol copolymer adhered between adjacent adherent layers consisting essentially of a partially hydrolyzed vinyl acetate polymer or copolymer. A layer of another material such as polypropylene can overlie the partially hydrolyzed vinyl acetate layers. The patent discloses co-extrusion of the EVOH and the partially hydrolyzed vinyl acetate polymer to form the multi-layer structure and then subsequent co-extrusion of the overlying material onto this structure. The patent does not suggest that this construction could be biaxially oriented and is otherwise distinguishable from the present invention because the adhesive is different, it does not mention controlling crystallinity of the EVOH, the percent ethylene of the products mentioned is too low for flexibility for biaxially oriented film, and, even if this film was to be biaxially oriented, the operation would be a two-step operation whereas the operation of the present invention is a one-step operation.

### SUMMARY OF THE INVENTION

The present invention relates to a method of producing a biaxially oriented oxygen and moisture barrier film which comprises first co-extruding at least one polyole-

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fin layer of a polyolefin selected from the group consisting of polyethylene, polypropylene and copolymers of ethylene with other olefin monomers, at least one layer of an ethylene vinyl alcohol copolymer with a melt flow rate of at least about 8 grams per 10 minutes, and at least one adhesive layer wherein these layers are combined into a composite sheet with the adhesive interposed between the core layer and the EVOH. Next, the composite sheet is immediately cooled so that the crystallinity of the EVOH is no more than about 25%. Finally, the composite sheet is biaxially oriented in the longitudinal direction to a degree of about 2:1 to about 4:1 and in the transverse direction to a degree of about 3:1 to about 7:1. In a preferred embodiment of the invention, the ratio of the thickness of the adhesive to the thickness of the core layer is about 1:8 to about 1:15. The invention also relates to a biaxially oriented oxygen and moisture barrier film formed by the above method.

### DETAILED DESCRIPTION OF THE INVENTION

The ethylene vinyl alcohol (EVOH) copolymers used in the present invention are the saponified or hydrolyzed product of an ethylene-vinyl acetate copolymer having, generally, an ethylene content of 25 to 75 mole percent. It is highly preferred that the percent ethylene in the EVOH be at least 45 percent so that the EVOH is flexible enough to be stretched during the orientation process. The degree of hydrolysis should reach at least 96 percent, preferably at least 99 percent. It is highly preferred that the degree of hydrolysis be greater than 96 percent because below that the barrier properties are less than optimum. It is extremely important to the performance of the present invention that the melt flow rate of the EVOH be at least 8 grams per 10 minutes at 190° C. and a load of 2,160 grams. If the melt flow rate is less than 8 grams per 10 minutes then the viscosities of the EVOH, adhesive, and core layer cannot be matched. It is important to match the viscosities of these materials to avoid interfacial instability which causes waviness of the melt and uneven distribution of the layers, otherwise known as melt fracture. The viscosity of these materials is most easily and effectively matched by monitoring the melt flow rate of the materials. At EVOH melt flow rates below 8 grams per 10 minutes, melt fracture occurs. It does not occur if the melt flow rate is higher.

The polyolefin layer used in the present invention can be of a polyolefin selected from the group consisting of polyethylene, including low density polyethylene, high density polyethylene, and linear low density polyethylene, polypropylene, and copolymers of ethylene with ~~olefins~~ <sup>propylene</sup>. The preferred polymers for use as the polyolefin layer are polypropylene and ethylene propylene copolymers containing predominately propylene. The melt flow rate of the polyolefin layer must not be so low that it is too stiff and thus unorientable. For propylene ethylene copolymers, it is preferred that the melt flow rate be from about 2.5 to about 6.0 grams per 10 minutes at 230° C. and a load of 2,160 grams. For polypropylene, it is preferred that the melt flow rate be from about 2.5 to about 4.5. In this range, the viscosities of the copolymer and the polypropylene are most compatible with EVOH and the adhesive. Also, in this range, orientation of the copolymer or the polypropylene results in the best properties.

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The adhesive used in the present invention should be selected from the group consisting of maleic anhydride-modified polymers and polymers similar thereto. Such polymers are effective adhesives for adhering the polyolefin layer to the EVOH layer and also a viscosity similar to the above-described EVOH and polyolefin layers. The preferred adhesives for use in this invention are maleic anhydride-modified polyolefins. Examples of such polymers are the Admer® QF-500 series manufactured by Mitsui Petrochemical Company, the Modic® P-300 series manufactured by Mitsubishi Petrochemical Company, and Plexar® adhesives manufactured by Chemplex.

The process for the manufacture of a biaxially oriented three or more layer composite barrier sheet consists of four distinct steps, which together comprise a relatively simple continuous operation. First, the composite sheet, consisting of polypropylene, for example, an adhesive layer, and an EVOH barrier layer, is formed by co-extrusion of the above components. One way of accomplishing this is to use three extruders and have the materials fed into a combining feed block. Within the feed block, the materials are layered to form the multi-layer melt stream wherein the adhesive is interposed between the polypropylene and the EVOH. The melt stream is fed into a slot cast sheet die or other type of die to form the multi-layer sheet. As the sheet exits the die, it is immediately cooled by use of a cooling drum or a water bath to a temperature satisfactory to maintain a 25 percent crystallinity rate in the EVOH material.

The 25 percent crystallinity rate can be obtained by maintaining the temperature of the cooling medium at 30° to 40° C. If the crystallinity of the EVOH is higher than 25 percent at this point in the process, the EVOH becomes too stiff to stretch properly in the orientation process and it will merely break apart. It is preferable that the crystallinity of the EVOH should be at least about 20 percent in order to obtain sufficient crystallinity in the final product.

Immediately after cooling, the composite sheet is fed into an apparatus adapted for biaxial orientation of plastic material. Any such apparatus can be used in the present invention. One example would be to feed the composite sheet into a set of differential speed heated rollers to stretch the sheet in the longitudinal direction to a degree of about 2:1 to about 4:1. Next, the sheet can be fed to a tenter frame where it is stretched in the transverse direction to a degree of about 3:1 to about 7:1.

If the degree of longitudinal orientation is less than about 2:1, then uneven orientation occurs, and if it is more than about 4:1, then fracture of the sheet occurs. If the degree of orientation in the transverse direction is less than about 3:1, then uneven orientation occurs, and more than about 7:1, then fracture of the sheet occurs. If polypropylene is used as the polyolefin layer, then it is preferred that the machine direction orientation rollers be at a temperature of from about 130° to about 140° C. and that the tenter frame for transverse orientation be at about 150° to about 160° C. If propylene ethylene copolymers are used in the polyolefin layer, then the machine direction roller temperature should be about 125° to about 130° C. and the tenter frame temperature should be about 130° to about 135° C.

After the sheet has been biaxially oriented, it is subjected to a heat setting treatment which allows the EVOH to crystallize. The crystallizing of the EVOH

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imparts high barrier properties to the EVOH layer and thus to the composite film. Any known heat setting method can be used, but one example of such a method is to pass the biaxially stretched sheet over a series of heated rolls.

It is highly preferred that the ratio of the thickness of the adhesive to the thickness of the polyolefin layer be about 1:8 to about 1:15. If the ratio is less than about 1:8, then poor adhesion between the EVOH and adhesive occurs, preventing satisfactory orientation. If the ratio is more than about 1:15, then uneven flow distribution of the adhesive occurs and the adhesion is poor.

#### EXAMPLES

The materials used in all of the following examples are:

##### Polypropylene:

Homopolymer - Solvay Eltex HP405, 3.8 melt flow rate

Copolymer - Solvay KS400, 5.7 melt flow rate (4% ethylene, 96% propylene)

##### Ethylene Vinyl Alcohol Copolymer:

Eval® "F" Grade resin made by Kuraray Co., Ltd. - 1.5 melt index

EVAL® "E" Grade resin made by Kuraray Co., Ltd. - 5.6 melt index

EVAL® "G" Grade resin made by Kuraray Co., Ltd. - 15.1 melt index

##### Adhesive:

Admer® QF500B - 4.2 melt flow rate (a maleic anhydride-modified polypropylene)

All of the following examples attempted to produce a biaxially oriented five layer composite barrier sheet of ABCBA construction according to the same general process consisting of the following four distinct steps:

1. A five layer composite sheet was co-extruded by the use of three extruders. The sheet consisted of a polyolefin (A layer), an adhesive layer (B layer), an EVOH layer (C layer), another adhesive layer (B layer), and another polyolefin layer (A layer). The materials were fed into a combining feed block where they were layered to form the five layer melt stream of ABCBA construction. This melt stream was then fed into a slot cast sheet die to form the five layer sheet. As the sheet exited the die, it was immediately cooled by the use of a cooling drum, or in some cases a water bath, to a temperature which maintained a 25 percent crystallinity rate in the EVOH material.

2. Immediately after cooling, the composite sheet was fed into a set of differential speed heated rolls (MDO) which stretched the sheet in the longitudinal direction.

3. After exiting the differential speed heated rollers (MDO), the sheet was fed to a tenter frame. In the tenter frame, the sheet was stretched in the transverse direction.

4. After the sheet was biaxially stretched, it was passed over a series of heated rolls which imparted a heat setting to the composite sheet and allowed the EVOH layer to crystallize. The crystallizing of the EVOH imparted high barrier properties to the composite sheet.

The following examples specify which materials were used. The orientation of the extruders was as follows in all cases:

Extruder #1: Always polypropylene

Extruder #2: Always EVOH

Extruder #3: Always Adhesive

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## EXAMPLES

In all cases in the following examples, the crystallinity of the EVOH material as it exited the die was maintained below 25%. The crystallinity ranged from 18 to 22% in the examples. The method of determination of the percent crystallinity is based upon the linear relationship between the percent crystallinity and the density of the film. The percent crystallinity is empirically determined by measuring the density of the total amorphous portion and the total crystalline portion of a particular grade of EVOH film and using this information in the formula set out below.

The density is first measured by any acceptable method such as ASTM D1505-68. Next, the total amorphous and total crystalline portions of the EVOH are separated and their densities measured according to the same procedure. For the three grades of EVOH used in the following examples, the densities of the amorphous and crystalline portions are as follows:

TABLE

Grade	Density of Amorphous Portion	Density of Crystalline Portion
E Grade	1.110	1.148
F Grade	1.163	1.200
G Grade	1.094	1.130

The above densities are considered constants because they do not change. The film density will change depending upon the degree of the quenching treatment. In the following formula FD is the film density, AD is the amorphous density constant, and CD is the crystalline density constant. The percent crystallinity of a film is determined by:

$$\% \text{ Crystallinity} = \frac{FD - AD}{CD - AD} \times 100$$

Thus, it is clear that the percent crystalline increases linearly as the density of the film increases. The crystallinity of the film can be controlled by controlling the density of the film. This is what takes place in the quenching step.

## EXAMPLE I

Materials:	Homopolypropylene
	EVOH "E" Grade
Extruder #1:	Adhesive
Extruder #2:	Melt Temp. 260° C., RPM
Extruder #3:	(revolutions per minute) 117.5
Feedblock Temperature:	Melt Temp. 190° C., RPM 25
MDO Rolls Temperature:	Melt Temp. 185° C., RPM 29.5
Tenter Temperature:	200° C.
MDO Orientation:	120° C.
Transverse Orientation:	165° C.
	2.0:1
	3.0:1

The stretched film exhibited a fishnet effect due to the fibrillation of the EVOH layer.

## EXAMPLE II

Using the same conditions and materials as in Example I, except that the RPM of Extruder #2 (EVOH) was reduced to 15 and the machine direction (MD) orientation was increased to 3.0:1, the same fishnet appearance was evident.

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## EXAMPLE III

Starting with the conditions and materials in Example II, the degree of MD orientation was varied while the transverse direction (TD) orientation was held constant. As the MD orientation was decreased from 3.0:1 to 2.0:1, the fishnet appearance decreased. At a 1.0:1 MD orientation and a 3.0:1 TD orientation, the fishnet appearance disappeared. This, however, only resulted in a uniaxially (transverse direction) oriented sheet which exhibit non-uniform thickness and poor optical properties:

## EXAMPLE IV

In observing the samples from Example I through III, it was noted that the reason for the fibrillation of the EVOH layer might have been due to the lack of adhesion between the PP and EVOH layers. To investigate this, the conditions and materials used in Example I were selected as a base point. The melt temperature of the adhesive layer was increased in increments of 5° C. until the melt temperature was the same as that of the polypropylene. It was noted that the adhesion became better as the temperature was increased. However, fibrillation of the EVOH layer was still present.

## EXAMPLE V

Materials:	Copolymer Polypropylene
	EVOH "E" Grade
Extruder #1:	Adhesive
Extruder #2:	Melt Temp. 240° C., RPM 95
Extruder #3:	Melt Temp. 190° C., RPM 15
Feedblock Temperature:	Melt Temp. 260° C., RPM 50
MDO Rolls Temperature:	180° C.
Tenter Temperature:	120° C.
MDO Orientation:	165° C.
Transverse Orientation:	2.4:1
	4.0:1

The initial trials exhibited minor fibrillation of the EVOH layer and uneven orientation of the polypropylene layer. The RPM of the EVOH layer were increased to 30 to increase the thickness. Fibrillation still resulted. The thicknesses of the various layers were increased in increments of 0.5 times the original up to two times the original. There was no appreciable effect on fibrillation. Orientation temperatures were varied until a limit on the low end was reached where transverse stretching would not occur and on the high end until the polypropylene would stick to the tenter frame clips. Fibrillation still was evident. The conclusion reached from the first five examples was that EVOH "E" grade could not be satisfactorily biaxially oriented.

## EXAMPLE VI

Materials:	Copolymer Polypropylene
	EVOH "E" Grade
Extruder #1:	Adhesive
Extruder #2:	Melt Temp. 240° C., RPM 95
Extruder #3:	Melt Temp. 185° C., RPM 20
Feedblock Temperature:	Melt Temp. 250° C., RPM 75
MDO Rolls Temperature:	115° C.
Tenter Temperature:	120° C.
MDO Orientation:	140° C.
Transverse Orientation:	2.8:1
	3.0:1



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The above conditions were the starting conditions. The composite sheet exhibited extreme melt fracture upon exit from the die. This melt fracture was occurring in the EVOH layer and was due to the difference in viscosities of the various components. The difference in viscosities in turn affected the flow properties through the feedblock and die. Various combinations of heat and speed were investigated until the following parameters were reached which in turn resulted in a satisfactory biaxially oriented composite sheet.

Extruder #1:	Melt Temp. 240° C., RPM 95
Extruder #2:	Melt Temp. 200° C., RPM 20
Extruder #3:	Melt Temp. 250° C., RPM 50
Feedblock Temperature:	200° C.
MDO Rolls Temperature:	129° C.
Tenter Temperature:	130° C.
MDO Orientation:	2.0:1
Transverse Orientation:	3.0:1

## EXAMPLE VII

Materials:	Homopolypropylene <del>EVOH-30G</del> Adhesive
Extruder #1:	Melt Temp. 260° C., RPM 115
Extruder #2:	Melt Temp. 190° C., RPM 20
Extruder #3:	Melt Temp. 250° C., RPM 80
Feedblock Temperature:	200° C.
MDO Rolls Temperature:	140° C.
Tenter Temperature:	150° C.
MDO Orientation:	4.4:1
Transverse Orientation:	3.0:1

Again, the above conditions were the starting conditions. Although the sheet going into the tenter frame looked good, holes were torn in the sheet during transverse orientation. This indicates either the sheet is too cold or the orientation is too high. Various orientation ratios were investigated from MDO 2.0:1 to 4.0:1 and transverse from 3.0:1 to 5.4:1. It was noted that as the MDO ratio was increased from 2.0:1, the EVOH started to fibrillate. At 4.0:1 MDO ratio, the EVOH was totally fibrillated. Increasing the transverse ratio and holding the MDO at 2.0:1 did not have the same effect.

## EXAMPLE VIII

In an attempt to match viscosities and flow rates of the various materials, the following changes were made in the conditions used in Example VII.

Extruder #1:	RPM 85
Extruder #2:	RPM 25
Extruder #3:	RPM 25
Tenter Temperature:	160° C.
MDO Orientation:	3.0:1
Transverse Orientation:	4.2:1

Using these conditions, an excellent biaxially oriented sheet was produced. The properties of this sheet are shown in the Table. Orientation ranges from MDO 2.0:1 to MDO 4.0:1 and transverse 3.0:1 to 7.0:1 were studied and satisfactory sheets were produced. The properties of two different films made hereunder are shown in the Table.

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## EXAMPLE IX

To further investigate the effects of parameters on the ability to orient the sheet, the following was studied:

To determine the effect of Adhesive thickness: The PP RPM was held constant. The adhesive RPM was decreased in 5 RPM increments to 25 RPM. At 25 RPM, fibrillation occurs.

To determine the effect of PP thickness: The adhesive RPM was held constant. The PP RPM was decreased to 70 RPM. Uneven flow distribution occurred. The adhesive RPM was set at 25 RPM. The PP RPM was 70. Uneven flow distribution occurred.

## EXAMPLE X

Materials:	Homopolypropylene <del>EVOH-30G</del> Adhesive
Extruder #1:	Melt Temp. 260° C., RPM 85
Extruder #2:	Melt Temp. 210° C., RPM 25
Extruder #3:	Melt Temp. 250° C., RPM 50
Feedblock Temperature:	210° C.
MDO Rolls Temperature:	140° C.
Tenter Temperature:	160° C.

MDO orientation from 2.0:1 to 3.0:1 and transverse orientation at 3.0:1 were attempted and fibrillated film resulted. Changes in Extruder #1 RPM to 80 and Extruder #2 RPM to 40 did not have any effect. Various temperature conditions did not have any effect. The conclusion was the EVOH "F" grade could not be satisfactorily biaxially oriented.

## Final Thickness

This is a determination of the thickness of even layer in the five layer composite sheet. The film was characterized by both light microscopy and scanning electron microscopy (SEM) techniques. For the SEM technique, the samples were notched and fracture. Light microscopy samples were imbedded in LDPE and microtomed in thin sections. By using the thickness of the individual layers, comparisons can be made between the properties of oriented and unoriented films of the same thickness.

O<sub>2</sub> Transmission

It is known that the presence of oxygen causes foods to degrade. The O<sub>2</sub> transmission of structure is a measure of its barrier to the penetration of oxygen to the materials packaged with the film structure. This determination was carried out according to ASTM Standard D3985-81.

## MVTR

The Moisture Vapor Transmission is an indication of the amount of H<sub>2</sub>O that will permeate to the packaged goods or conversely the amount of moisture that can escape from a packaged liquid product. Also the barrier properties of a barrier material are deteriorated by the presence of moisture. Therefore, it is desirable to prevent as much moisture as possible from reaching the barrier layer. This test was carried out according to ASTM Test Methods E938-70.

## Ultimate Tensile

The ultimate tensile strength is a measure of the strength of the material. It is the amount of force per square inch of material required to pull it apart. This test was carried out according to ASTM D-882-73, Method A.

## Secant Modulus



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The secant modulus is a measure of the stiffness of the material. A stiff material is required to provide good machineability and handling in subsequent packaging operations, and also to provide a crisp feel to packaged products. This method was carried out according to AS, M D-618.

TABLE

Example	Final Thickness	O <sub>2</sub> Transmission cc/m <sup>2</sup> /24 hrs. @ 20° C. 0% RH	MVTR g/m <sup>2</sup>	Ultimate Tensile		Secant Modulus	
				MD MPa	TD MPa	MD Mpa	TD Mpa
Homo-polymer PP	12	12	3.0	80	250	1888	5148
Adhesive EVOH	1.3						
G	3.5						
Adhesive Homo-polymer PP	1.3						
12							
Homo-polymer PP	13	13	3.3	91	238	1575	4089
Adhesive EVOH	1						
G	2						
Adhesive Homo-polymer PP	1						
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I claim:

1. A method of producing a biaxially oriented oxygen and moisture barrier film which comprises:

(a) co-extruding

(1) at least one layer of a polyolefin material selected from the group consisting of polyethylene, polypropylene, and copolymers of ethylene with other olefins,

(2) at least one layer of an ethylene vinyl alcohol copolymer with a melt flow rate of at least about 8 grams per 10 minutes, and

(3) at least one adhesive layer

and combining these layers into a composite sheet wherein the adhesive is interposed between the polyolefin layer and the ethylene vinyl alcohol copolymer layers,

(b) immediately cooling the composite sheet so that the crystallinity of the ethylene vinyl alcohol copolymer is no more than about 25 percent, and

(c) biaxially orienting the composite sheet in the longitudinal direction to a degree of about 2:1 to about 4:1 and in the transverse direction to a degree of about 3:1 to about 7:1.

2. The method of claim 1 wherein the ratio of the thickness of the adhesive to the thickness of the polyolefin layer is about 1:8 to about 1:15.

3. The method of claim 1 wherein the composite sheet is cooled in a cooling medium at a temperature of 30° to 40° C. in step (b).

4. The method of claim 1 wherein the longitudinal orientation is carried out at a temperature of from about 130° to about 140° C. and the transverse orientation is carried out at a temperature of from about 150° to 160°

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C. and the polyolefin layer is comprised of polypropylene.

5. The method of claim 1 wherein the longitudinal orientation is carried out at a temperature of from about 125° to about 130° C. and the transverse orientation is carried out at a temperature of from about 130° to 135° C. and the polyolefin layer is comprised of a copolymer of propylene and ethylene.

6. The method of claim 1 wherein the polyolefin layer is selected from the group consisting of polypropylene and copolymers of propylene and ethylene.

7. The method of claim 1 wherein a five layer film is produced comprising two outer polyolefin layers, an inner ethylene vinyl alcohol copolymer layer, and two adhesive layers disposed between the polyolefin layers and the ethylene vinyl alcohol copolymer layer.

8. A biaxially oriented oxygen and moisture barrier film formed by:

(a) co-extruding

(1) at least one layer of a polyolefin material selected from the group consisting of polyethylene, polypropylene, and copolymers of ethylene with other olefins,

(2) at least one layer of an ethylene vinyl alcohol copolymer with a melt flow rate of at least about 8 grams per 10 minutes, and

(3) an adhesive layer

and combining these layers into a composite sheet wherein the adhesive is interposed between the polyolefin layer and the ethylene vinyl alcohol copolymer layers,

(b) immediately cooling the composite sheet so that the crystallinity of the ethylene vinyl alcohol copolymer is no more than about 25 percent, and

(c) biaxially orienting the composite sheet in the longitudinal direction to a degree of about 2:1 to about 4:1 and in the transverse direction to a degree of about 3:1 to about 7:1.

9. The film of claim 8 wherein the ratio of the thickness of the adhesive to the thickness of the polyolefin layer is about 1:8 to about 1:15.

10. The film of claim 8 wherein there are five layers which are comprised of two outer polyolefin layers, an inner ethylene vinyl alcohol copolymer layer, and two adhesive layers disposed between the polyolefin layers and the ethylene vinyl alcohol copolymer layer.

11. The film of claim 8 wherein the polyolefin layer is selected from the group consisting of polypropylene and copolymers of propylene and ethylene.

12. The film of claim 8 wherein the composite sheet is cooled in a cooling medium at a temperature of 30° to 40° C. in step (b).

13. The film of claim 8 wherein the longitudinal orientation is carried out at a temperature of from about 130° to about 140° C. and the transverse orientation is carried out at a temperature of from about 150° to 160° C. when polypropylene is the core layer.

14. The film of claim 8 wherein the longitudinal orientation is carried out at a temperature of from about 125° to about 130° C. and the transverse orientation is carried out at a temperature of from about 130° to about 135° C. when the core layer is a copolymer of propylene and ethylene.

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**United States Patent** [19]  
**Krueger et al.**

[11] **Patent Number:** 4,588,648  
 [45] **Date of Patent:** May 13, 1986

[54] **MULTIPLE LAYER PLASTIC FILM HAVING  
 POLYPROPYLENE ADHERED TO NYLON**

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[21] **Appl. No.:** 635,630

[22] **Filed:** Jul. 30, 1984

**Related U.S. Application Data**

[60] Division of Ser. No. 417,674, Sep. 13, 1982, Pat. No.  
 4,552,714, and a continuation-in-part of Ser. No.  
 236,601, Feb. 20, 1981, Pat. No. 4,361,628.

[51] **Int. CL<sup>4</sup>** ..... B32B 27/08

[52] **U.S. Cl.** ..... 428/475.8; 428/476.1;  
 428/516; 264/176 R

[58] **Field of Search** ..... 428/516, 476.1, 475.8

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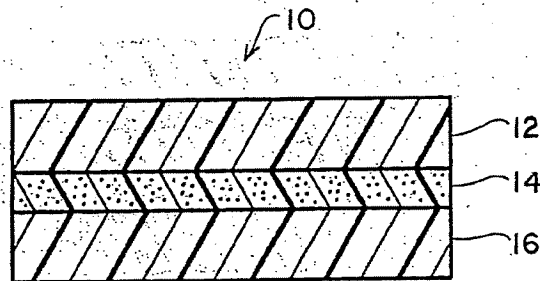
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*Primary Examiner*—P. C. Ives  
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 Wilhelm

[57] **ABSTRACT**

A novel coextruded plastic film has, as an adhesive layer between polypropylene and nylon layers, a blend of polypropylene and a graft copolymer of maleic anhydride onto an olefin polymer or copolymer, the adhesive blend containing from about 0.005% to 0.75% maleic anhydride based on the total weight of the entire blend composition.

7 Claims, 2 Drawing Figures



U.S. Patent

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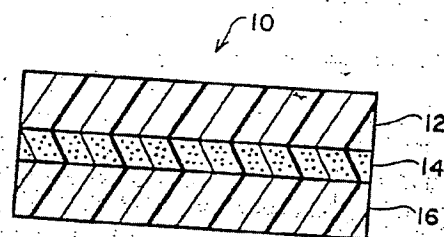


FIG. 1

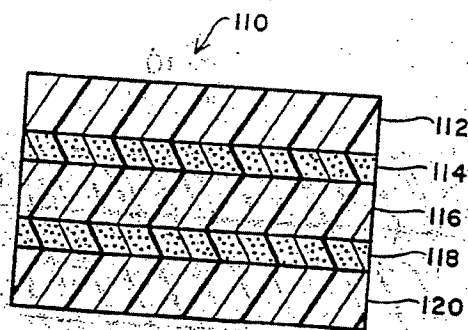


FIG. 2

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# MULTIPLE LAYER PLASTIC FILM HAVING POLYPROPYLENE ADHERED TO NYLON

This is a continuation-in-part of application Ser. No. 236,601, filed Feb. 20, 1981, issued as Pat. No. 4,361,628 on Nov. 30, 1982, for COEXTRUDED FILM OF POLYPROPYLENE, POLYPROPYLENE BLEND, AND NYLON, By Duane A. Krueger et al and a divisional of application Ser. No. 417,674, filed Sept. 13, 1982, now U.S. Pat. No. 4,552,714.

## BACKGROUND OF THE INVENTION

This invention pertains to coextruded plastic films, and particularly, to those films having a polypropylene layer adhered to a layer of a nylon-type polyamide. In such films, the adhesion between the nylon and polypropylene layers has been particularly troublesome. It has been surprisingly found that an excellent adhesive for the coextrusion of nylon and polypropylene is a blend of a graft copolymer of maleic anhydride onto an olefin polymer or copolymer and an ungrafted propylene-based polymer. The graft copolymer typically contains from about 0.10% to about 2.5% maleic anhydride based on the total weight of the graft copolymer, and must contain from about 0.005% to 0.75% maleic anhydride based on the total weight of the entire blend composition.

In the coextrusion of a 5-layer film, the structure may include a fourth layer, of ethylene vinyl alcohol copolymer (EVOH), affixed on one of its surfaces to the nylon, and a fifth layer, of nylon, affixed to the other surface of the EVOH.

Thus the process comprises coextruding polypropylene, and nylon with the adhesive blend juxtaposed therebetween. In the formation of a five layer structure containing EVOH, the process comprises coextruding the five layer structure of, in sequential order in the structural layering, from one outside surface to the other: polypropylene, adhesive blend, nylon, EVOH, and nylon.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-section of a three layer coextruded structure of this invention.

FIG. 2 is a cross-section of a five layer coextruded structure of this invention.

## DETAILED DESCRIPTION OF THE INVENTION

The most basic form of the invention is shown in the coextruded structure of FIG. 1, which is generally designated 10. The structure has three layers which are, respectively, a polypropylene layer 12, an adhesive blend layer 14 of a maleic anhydride graft copolymer of an olefin and an ungrafted polypropylene, and a nylon layer 16.

Layer 12 may be polypropylene homopolymer, a propylene ethylene copolymer, or a blend of polypropylene and polyethylene. In any event, the ethylene content may be up to about 50% by weight of the layer 12 composition. The polymer resin, or blends of resin, must, of course, be extrudable polymers. A preferred polymer for layer 12 is sold under the tradename of Hercules SA-752, which also contains about 4% ethylene. Another suitable polymer is Eastman 4G7DP, which contains small amounts of ethylene vinyl acetate.

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Layer 16 is a polymer, copolymer, or blend thereof selected from the nylon family of polyamides. Very desirable polymeric compositions for layer 16 are nylon 6, nylon 66, and nylon 6,66, blends of nylon 6 with less than 25% nylon 12, and blends of at least about 75% nylon 6. Examples of materials which can be processed with nylon 6 as a blend are high density polyethylene, medium density polyethylene, or low density polyethylene and polypropylene. In general, any extrudable polymer may be satisfactorily used in a blend with the nylon so long as it neither degrades at the processing temperature of about 500° F. to about 530° F., nor reacts appreciably with the nylon 6.

Less desirable, but acceptable, are copolymers of nylon 6 and nylon 12. Unacceptable for layer 16 is nylon 12.

Processing additives such as slip agents and the like may be satisfactorily used.

Layer 14 serves as a coextruded adhesive layer between layers 12 and 16. It forms a strong bond with both layers 12 and 16. Layer 14 is a blend of two components: (1) a grafted copolymer of an olefin and maleic anhydride and (2) an ungrafted propylene-based polymer. The ungrafted propylene-based polymeric component (2) may be a polypropylene homopolymer, a propylene ethylene copolymer, or a blend of polypropylene and polyethylene. In any event, the ethylene content may be up to about 50% by weight of the ungrafted propylene-based component (2) of the blend. The term "ungrafted" as used herein limits the polymer in the sense that no significant anhydride moieties have been grafted thereon. Other polymeric grafts may optionally be present.

The grafted copolymer component (1) of the blend has a backbone, or chain, comprising an olefinic polymer or copolymer, with units of maleic anhydride having been grafted thereonto. For use in this invention, the graft copolymer component of the blend typically will contain from 0.1% to 2.5% maleic anhydride based on the total weight of the graft copolymer. One such graft copolymer suitable for use in this invention as component (1) of the blend is sold by Hercules Chemical Company as Hercoprime A-35. Other suitable copolymers based on propylene are sold by Mitsui Company, Japan, as QF-500 and QF-500X. Still other polymers are based on ethylene, such as ethylene copolymers and ethylene blends. Representative of these materials are those available from Chemplex Company under the Plexar tradename and from DuPont Company under the designation CXA.

The formulations of layers 12 and 14 may be advantageously effected by formulating polymeric compositions for layers 12 and 14 which compositions have similar basic polymeric structure. Thus, if it is found advantageous to have a high fraction of ethylene in layer 12, then the overall fraction of ethylene in layer 14 is advantageously greater than in cases where the ethylene fraction in layer 12 is relatively smaller.

While the ethylene content of the grafted copolymer is advantageously selected with regard to the ethylene contents of layer 12 and of the ungrafted polypropylene component, ethylene contents up to about 20% of the grafted copolymer may be used with any of the combinations of layer 12 composition and ungrafted copolymer composition. Ethylene contents between 20% and 50% of the grafted copolymer are used with compositions of ungrafted polypropylene component and layer 12 which include larger fractions of ethylene moieties.



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The blend for coextrusion as layer 14 in the coextruded structure is typically from about 5% to about 30% by weight of the maleic anhydride grafted copolymer, preferably about 5% to about 10%, and from about 70% to about 95% of the ungrafted polypropylene, preferably about 90% to about 95%. Most significantly, overall maleic anhydride concentration in the blend layer 14, based on the entire blend composition, is from about 0.005% to about 0.75%, with a preferred maleic anhydride concentration range of about 0.005% to about 0.25%. To the extent the anhydride modification may be different from the iterated 0.1% to 2.5%, the fraction of the grafted copolymer in the blend is adjusted so that the anhydride concentration in the overall adhesive blend composition is within the above iterated percentage.

In the preferred extrusion process the components of the individual layers are fed into extruders of like number, each extruder handling the material for one of the layers. As in the case of the five layer structure, illustrated, where two layers are identical, one extruder may handle the two identical layers. The melted and plasticated streams from the individual extruders are fed into a multiple manifold coextrusion die. The layers are juxtaposed and combined in the die, and exit the die as a single multiple layer film of polymeric material.

After exiting the die, the polymeric material is cast onto a first controlled temperature roll, passes around the first roll, and thence onto a second controlled temperature roll, which is normally cooler than the first roll. The controlled temperature rolls largely control the rate of cooling of the film after it exits the die. Typical operating temperatures for the first and second controlled temperature rolls are 160° F. and 120° F. respectively.

In another embodiment of the invention illustrated in FIG. 2, a five-layer structure is coextruded, wherein similar 100 series numbers represent similar layers in FIG. 1. Thus the entire structure is generally designated 110. Layers 112, 114, and 116 have the same compositions, and serve the same functions as layers 12, 14, and 16 respectively in FIG. 1. Layer 118 is a material providing an effective barrier to gaseous transmission, such as EVOH. Layer 120 is a layer of nylon, and may be any nylon which may be coextruded with the gas barrier material.

#### EXAMPLE 1

Five parts by weight of Hercoprime A-35 particles were blended with 95 parts by weight of pelletized Hercules SA-752 ungrafted polypropylene polymer to form the adhesive blend composition. A three layer film was cast coextruded through a 3-manifold cast die fed by three extruders processing, respectively, nylon 6, the above recited blend, and Hercules SA-752 polypropylene. Die temperature was 500° F. Line speed was 60 feet per minute. The film was cast onto a first controlled temperature chill roll maintained at 160° F., and passed from there onto a second chill roll at 120° F. The final film was 4.5 mils thick. The outer layers were 3.5 mils SA-752 polypropylene and 0.5 mil nylon, with a 0.5 mil layer of the blend serving as the adhesive layer between them.

#### EXAMPLE 2

A three layer 4.5 mil film was cast coextruded as in EXAMPLE 1, using as the nylon layer a blend of 75% Nylon 6 and 25% Nylon 12.

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#### EXAMPLE 3

A three layer, 4.5 mil, film was cast coextruded as in EXAMPLE 1, using as the adhesive blend a composition of 10 parts by weight Hercoprime A-35 and 90 parts by weight SA-752.

#### EXAMPLE 4

A three layer, 4.5 mil, film was cast coextruded as in EXAMPLE 2, using as the adhesive blend a composition of 10 parts by weight Hercoprime A-35 and 90 parts by weight SA-752.

#### EXAMPLE 5

Five parts by weight of Hercoprime A-35 particles were blended with 95 parts by weight of pelletized Hercules SA-752 polypropylene to form the adhesive blend composition. Using four extruders, a 3-manifold cast die, and a combining head, a five layer film was cast coextruded. One extruder fed an SA-752 polypropylene stream into the die. Another extruder fed a stream of the adhesive blend into the die. The third stream was generated by two extruders feeding the nylon and EVOH into the combining head. In the combining head, the extrudates from the two extruders were combined into a three-layer stream having nylon on its outer portions and a core layer of EVOH. Combining head temperature was 500° F. The three-layer stream was fed from the combining adaptor into the 3-manifold die, where it was juxtaposed, and finally, joined with the adhesive blend layer. Die temperature was 500° F. The final five-layer film was cast onto a first controlled temperature chill roll maintained at 160° F., and passed from there onto a second chill roll at 120° F. Line speed was 60 feet per minute. The final film was 5 mils thick and had the following distinct layers, in order:

polypropylene: 3.5 mils  
adhesive blend: 0.5 mil  
Nylon 6: 0.25 mil  
EVOH: 0.5 mil  
Nylon 6: 0.25 mil

#### EXAMPLE 6

A five-layer, 5 mil, film was cast coextruded as in EXAMPLE 5, using, as the nylon layers, a blend of 75% Nylon 6 and 25% Nylon 12.

#### EXAMPLE 7

A five-layer, 5 mil, film was cast coextruded as in EXAMPLE 5, using as the adhesive blend a composition of 10 parts by weight Hercoprime A-35 and 90 parts by weight SA-752.

#### EXAMPLE 8

A five layer, 5 mil, film was cast coextruded as in EXAMPLE 6, using as the adhesive blend a composition of 10 parts by weight Hercoprime A-35 and 90 parts by weight SA-752.

The adhesive bond between layers 14 and 16 was measured as peel strength in pounds per one inch width strip of specimen. In preparation for the peel test, specimens were cut into one inch strips. They were then tested in a Chatillon tester, manufactured by John Chatillon and Sons, N.Y. Crossing head speed was 10 inches per minute. The resulting peel strengths of all the samples were 2 lbs./in. width, with a range of 1.8 to 2.1 lb./in. width.

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Having thus described the invention, what is claimed is:

1. A multiple layer plastic film, comprising:

(a) a layer of polypropylene;

(b) a layer of nylon; and

(c) a functionally adhesive layer juxtaposed between said nylon layer and said polypropylene layer, said adhesive layer being a blend consisting essentially of (i) a graft copolymer of maleic anhydride onto an olefin polymer or copolymer and (ii) an ungrafted propylene-based polymer; and adhesive blending containing from about 0.005% to 0.75% maleic anhydride based on the total weight of the entire blend composition.

2. A plastic film as in claim 1 wherein the polypropylene layer in subparagraph (a) contains polyethylene up to about 50%.

3. A plastic film as in claim 1 and including an additional layer of ethylene vinyl alcohol copolymer affixed on one of its surfaces to said nylon, and a further layer of nylon affixed to the other surface of said ethylene vinyl alcohol copolymer.

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4. A plastic film as in claim 2 and including an additional layer of ethylene vinyl alcohol copolymer affixed on one of its surfaces to said nylon, and a further layer of nylon affixed to the other surface of said ethylene vinyl alcohol copolymer.

5. A plastic film as in claim 1 wherein said ungrafted propylene-based polymer contains less than 20% ethylene moieties by weight and wherein said graft copolymer contains 0.1% to 2.5% maleic anhydride based on the total weight of the graft copolymer, said graft copolymer comprising between about 5% and 30% by weight of the blend, and said ungrafted propylene-based polymer comprising between about 70% and 95% by weight of the blend.

6. A plastic film as in claim 5 wherein the polypropylene layer in subparagraph (a) contains up to about 50% ethylene.

7. A plastic film as in claim 5 and including an additional layer of ethylene vinyl alcohol copolymer affixed on one of its surfaces to said nylon, and a further layer of nylon affixed to the other surface of said ethylene vinyl alcohol copolymer.

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TO SEPARATE, HOLD TOP AND BOTTOM EDGES, SNAP-APART AND DISCARD CARBON

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(64) Heat-shrinkable laminate tubular film and process for producing it.

(65) Heat-shrinkable laminate tubular film comprising a gas-barrier layer of a copolymer of vinylidene chloride of thickness not less than 6  $\mu$ m and not more than 30% of the total thickness of the film, outer layers of polyolefin, at least one intermediate layer of a polyamide or a thermoplastic polyester both having a crystal melting point of not more than 240°C and have a thickness of 5 to 40% of the total thickness of the film, and adhesive layers disposed between any of the above layers.

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HEAT-SHRINKABLE LAMINATE TUBULAR FILM  
AND PROCESS FOR PRODUCING IT

The present invention relates to a heat-shrinkable laminate tubular film showing an adequate rigidity and a favorable stretchability.

More in detail, the present invention relates to a heat-shrinkable laminate tubular film comprising a gas-barrier layer of a copolymer of vinylidene chloride, outer layers of a polyolefin, at least one intermediate layer of a polyamide or a thermoplastic polyester both of which show a crystal melting point of not more than 240°C and have a specified thickness, and adhesive layers disposed between any of the above layers.

For packaging foodstuffs of non-uniform and irregular shape, a method of heat-shrink packaging is generally applied, and since the thus packaged foodstuff should be preserved safely for a long period, it is necessary that the packaging used is impermeable to gases, particularly to gaseous oxygen, in other words, the packaging material must have a gas-barrier property.

As the heat-shrinkable gas-barrier film for packaging foodstuffs, a single film of a copolymer of vinylidene chloride (hereinafter referred to as VDC) has been utilized. However, because of the poor mechanical properties of the single

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film of VDC at low temperatures, a composite laminate film comprising a gas-barrier layer of VDC and an outer layer of polyolefin has been developed. For instance, Japanese Patent Application Laying-Open No. 58-128821 (1983) discloses a laminate film comprising a gas-barrier layer of VDC and outer layers of a copolymer of ethylene and vinyl acetate (hereinafter referred to as EVA), and the disclosed film has solved the problem of the poor mechanical properties at low temperatures. However, because of the lack of rigidity in such a film, such a laminate film cannot exhibit a satisfactory operational processability in packaging foodstuffs.

In a first aspect of the present invention, there is provided a heat-shrinkable laminate tubular film comprising a gas-barrier layer of a copolymer of vinylidene chloride having a thickness of not less than 6  $\mu\text{m}$  and not more than 30% of the total thickness of the tubular film, outer layers of a polyolefin, at least one intermediate layer of a polyamide or a thermoplastic polyester having in either case a crystal melting point of not more than 240°C and a thickness of 5 to 40% of the total thickness of the tubular film, and adhesive layers disposed between any of the above layers.

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In a second aspect of the present invention, there is provided a process for producing a heat-shrinkable laminate film, comprising

feeding a copolymer of vinylidene chloride as a gas-barrier layer, a polyolefin as outer layers, a polyamide or a thermoplastic polyester as at least one intermediate layer and an adhesive material as adhesive layers to an annular die provided with passages for the gas-barrier layer, the outer layers, the intermediate layer(s) and the adhesive layers and with adiabatic spaces disposed on the both sides of the passage(s) of the intermediate layer(s), in a molten state, the end portions of the passages of the gas-barrier layer, the outer layers, the intermediate layer(s) and the adhesive layers emerging into a common outlet of the annular die.

laminating and extruding the copolymer of vinylidene chloride, the polyolefin, the polyamide or the thermoplastic polyester and the adhesive material, thereby forming laminate tubular film at the outlet of the annular die,

cooling the resultant laminate tubular film by quenching, and

after heating the laminate tubular film, biaxially stretching the resultant laminate tubular film, thereby forming a heat-shrinkable laminate tubular film.

In the attached drawing, Fig. 1 is a vertical cross-sectional view of the annular die, particularly the junction part thereof where streams of all the layers of the film are assembled.

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Since the gas-barrier layer of a VDC of the heat-shrinkable laminate tubular film according to the present invention is relatively thick, the retention time of the VDC in a passage of the die is relatively short and accordingly, there is the merit of scarcely causing thermal decomposition of the VDC in the production of the laminate tubular film.

Further, since the heat-shrinkable laminate tubular film according to the present invention has at least one intermediate layer of the polyamide or the thermoplastic polyester having a specified thickness, the laminate tubular film according to the present invention shows an adequate rigidity thereby overcoming difficulties due to elongation of the laminate tubular film caused by the weight of the article to be packaged in the packaging operation. In addition, the laminate tubular

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film according to the present invention exhibits more uniform stretchability than that of the laminate film disclosed in Japanese Patent Application Laying-Open No. 58-128821 (1983). The gas-barrier property of the laminate tubular film according to the present invention is of course excellent.

A VDC usable as the gas-barrier layer in a heat-shrinkable laminate tubular film according to the present invention comprises a copolymer of from 65 to 95% by weight of vinylidene chloride and from 5 to 35% by weight of at least one comonomer copolymerizable with vinylidene chloride. As the comonomer copolymerizable with vinylidene chloride, for instance, vinyl chloride, acrylonitrile and,  $C_1$  to  $C_{18}$ -alkyl acrylates may be mentioned. Of these comonomers, vinyl chloride is generally used. The VDC may contain a small amount of plasticizer(s) and/or stabilizer(s) according to necessity. These additives, i.e., the plasticizers and stabilizers, used in the present invention have been known by the persons skilled in the art and represented by, for example, dioctyl adipate and epoxidized soy-bean oil.

As has been stated, it is necessary that the thickness of the gas-barrier layer of the VDC is not less than  $6\mu m$  and is not more than 30%, preferably not more than 25% of the total thickness of the laminate tubular film according to the present invention. If below  $6\mu m$ , the retention time thereof in the passage of the die becomes so large in extruding the VDC with the polyamide or the thermoplastic polyester in lamination that the VDC decomposes, thereby giving difficulty in co-extrusion.